Random Acrylate Copolymer Surface Grafting to Poly(dimethyl siloxane) Elastomer Surfaces for Improved Anti-Biofouling

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Statement of Purpose: Biofouling of surfaces in liquid environments affect a wide variety of sectors such as maritime shipping, aquaculture, water treatment plants, power generation stations, and medical devices. Fouling vectors include a wide variety of marine organisms, cells, and proteins [1]. In order to tackle this complex problem, various strategies to control the response of the fouling vector have been developed such as engineered microtopographies and chemical surface modification [1]. Poly(ethylene glycol) (PEG) grafted surfaces have long been know to be effective antifouling surfaces; however, PEG surfaces suffer from poor longevity [2]. Control of the graft molecular weight and graft density have also been shown to be important factors [2]. It is hypothesized that acrylate copolymers will create effective antifouling surfaces because of the amphiphilic and charged nature of the chosen monomers, and the molecular weight of the grafts will have a marked impact on the biofouling response.

Methods: Random copolymers composed of acrylic acid, acrylamide, and methyl acrylate in a 3:3:4 molar ratio were chemically grafted to poly(dimethyl siloxane) elastomer (PDMSe) (Xiameter® Dow Corning) surfaces through the use of 3-mercaptopropyl trimethoxysilane as a silane coupling agent in conjunction with thiol chain transfer and surface initiated radical chain growth polymerization. Molecular weight of grafted chains was controlled with the addition of the chain transfer agent thioglycolic acid. This grafting process was used on topographically smooth surfaces and patterned surfaces containing the Sharklet™ (Sharklet Technologies, Inc. 12635 E. Montview Blvd., Suite 160, Aurora, CO 80045) engineered topography. Surface grafting was confirmed with contact angle, XPS, and FTIR-ATR analysis. GPC/SEC analysis was used to determine the molecular weight of the bulk polymer, and these values were used to estimate surface graft molecular weight. The biofouling response of the surfaces was investigated by analyzing the fouling and attachment density of the *Ulva linza* zoospore in artificial seawater, bovine serum albumin in PBS, and 3T3 mouse fibroblasts in growth media. Reduction in attachment density for grafted surfaces was compared using a smooth un-modified PDMSe control.

Results: Contact angle, FTIR-ATR, and XPS confirmed that the grafting process is successful at creating acrylate copolymer surface grafts to PDMSe surfaces. GPC analysis showed that by varying the chain transfer agent concentration from 0-20 mM, the M_w of the polymers was modified two orders of magnitude from approximately 1,050 to 10 kg/mol. Surfaces appear to be stable while stored in water for the maximum time tested of 7 months. Attachment density data for *Ulva linza* revealed a reduction of 75.4% for the high M_w graft and 86.7% for the low M_w graft. The addition of the Sharklet™ topography with low M_w graft caused an impressive reduction of 96.7%. Initial results with albumin attachment revealed that high M_w grafts cause a 45.4% reduction in settlement. Unfortunately, initial results indicate that high M_w grafted surfaces increase the attachment density of 3T3 fibroblasts. Additional experimentation is ongoing.

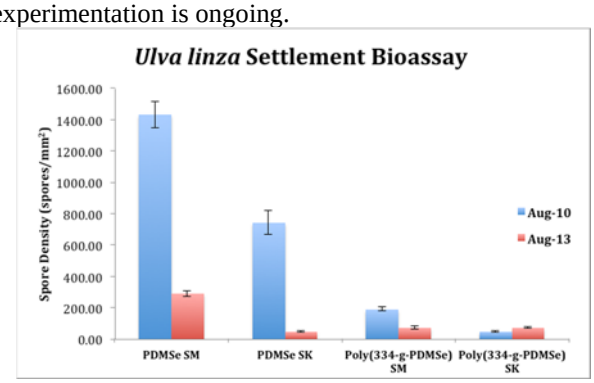

Figure 1. *Ulva linza* spore density data from two bioassays performed on smooth (SM) and Sharklet™ patterned (SK) with unmodified PDMSe and acrylate grafted poly(334-g-PDMSe). Aug-10 assay contains low M_w grafts, and Aug-13 assay contains high M_w grafts.

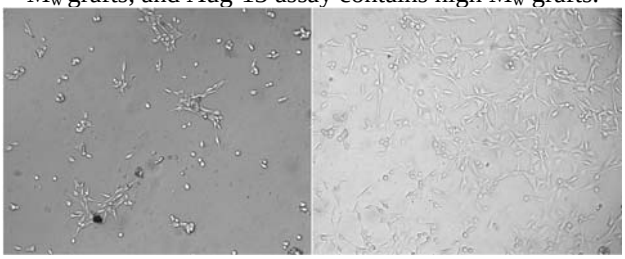

Figure 2. 100x phase contrast optical micrograph of 3T3 mouse fibroblast attachment assay on PDMSe control (left), and grafted poly(334-g-PDMSe) of high M_w (right).

Conclusions: The grafting process developed was successful at creating random copolymers composed of acrylic acid, acrylamide, and methyl acrylate to PDMSe surfaces with tailorable molecular weight. The acrylate surface grafts exhibited molecular weight dependence on the attachment response of the marine zoospore *Ulva linza* with a maximum reduction in attachment density of 96.7% obtained on patterned surfaces. Initial testing shows promising results with albumin attachment and less than ideal 3T3 fibroblast attachment. Acrylate grafts have been shown to create effective antifouling surfaces that are stable in water. Future work will include additional testing of the 3 discussed fouling vectors and fibronectin with a full study analyzing the effect of molecular weight on the biofouling response.

References:

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[2] Andruzzi LS. Langmuir. 2005;21:2495-2504